Restoration of Pure Silver from X-Ray film waste

H Rehana Anjum[1], T Noorjahan Begum[2], D Raja Kullayappa[3]

1. Department of Chemical Engineering, Jawaharlal Nehru Technological University College of Engineering Anantapur, Jawaharlal Nehru Technological University Anantapur, Ananthapuramu

2. Department of Chemistry, Jawaharlal Nehru Technological University College of Engineering Anantapur, Jawaharlal Nehru Technological University Anantapur, Ananthapuramu

3. Department of Mechanical Engineering, Jawaharlal Nehru Technological University College of Engineering Anantapur, Jawaharlal Nehru Technological University Anantapur, Ananthapuramu

Abstract

Silver is a depleted precious resource and in the near future it all be used up. In addition to this, our country is not produced the metal at this moment. Extracting silver from enough silver containing wastes like used X-ray photographic film will considerably save the foreign currency to import this metal. The waste X-ray photographic films containing 1.5-2% (w/w) black metallic silver would be used for recovery and reuse. Around 18-20% of the world's silver needs are supplied by recycling photographic waste. Extraction of silver from the ore is expensive and harmful to the environment. Global demand for silver remains steadily increasing from 25,700 metric tons in 2016 to 30,500 metric tons in 2021. Most photographic and X-ray wastes contain silver thiosulphate with silver at a concentration of 5 parts per million (ppm). Several technologies exist to recover silver from X-ray photographic film such as burning the film, electrolysis, metal replacement, chemical precipitation and bacterial, enzymatic methods. Except chemical methods, the other methods are expensive and time consuming to recover silver. The composition of X-ray film is plastic (60%), adhesive layer (3%), emulsion (Gelatin & silver halide)25%, super coat (toxic metal) 10%. The present study explores the recovery of high purity silver using different chemicals like nitric acid and Sodium hypochlorite (bleaching solution).

Keywords: Silver, X-ray photographic films, Sodium thiosulphate, Nitric acid, solution hypochlorite, Bleach solution.

1. Introduction:

Silver occurs from ores such as argentite and chlorargyrite (horn silver). However, it is mostly extracted from lead-zinc, copper, gold and copper-nickel ores as a by-product of mining for thesemetals. The metal is recovered either from the ore, or during the electrolytic refining of copper. World production is about 20,000 tons per year [1]. The first X-rays machine was discovered accidentally in 1895 by the German scientist Wilhelm Roentgen. X-ray is also a kind of radiation. They behave in much the identical way as light rays, but at much shorter wavelengths. X-radiation is made by taking energy from electrons and converting into photons with appropriate energies. The middle of an X-ray apparatus is an electrode pair a cathode and an anode. X-ray extremely short wavelength and high frequencywith wavelengths starting from about 10^{-8} to 10^{-12} metre and corresponding frequencies from about 10^{16} to 10^{20} hertz. Conventional fixing of AgX in photographic and X-ray films has been extensively employed in the photo-industry for over than two centuries [2]. In the United States, coin silver was once again a standard alloy. The "coin silver" technical alloy consists of 900 or 90% silver or 10% copper. The name "coin silver" comes from the fact that the metalworkers have historically manufactured items from scrap metal. The coins were made of precious metal. Monetary coins in our country are not silver and made of cheaper, more natural, basic metals. Some investment coins have higher silver content. They have a quality mark and usually come with authenticity certificates [3, 4].

Silver recovery from x – ray film is a technique in which at the end of it silver on x – ray is recovered in a purity of 99.8%of silver in order to reuse the silver on various applications [5]. Electrolysis is the most generally used and universally applicable method for silver recovery within the photo processing industry. Electrolytic silver recovery cell consists of a cathode and anode. Oxidation at the anode is positive and reduction at the cathode is negative. Silver is deposits on the cathode during electrolysis [6]. After sufficient silver has been plated, the cathode is removed from the system and also the silver stripped off. This method is capable to producing silver with purity greater than 98%. Raw material to be refined on the anode and the pure metal is deposited at the cathode [7]. A heavy current of up to 300 amperes is passed through the cell, and the silver is deposited as metallic silver at the cathode. Electrochemical cell experiments were carried out in a rectangular cell made of acrylic plates with groves cut along the sides to mount the electrodes at specific distance of separation between them [8].

2. Materials

The methodology consists of recovery of silver from waste x – ray films using different chemicals such as Nitric acid and Sodium hypochlorite.

The reaction mechanism involved in the conversion of x – rays to silver is ***Double Displacement*** reaction. The chemical process involved in the conversion of x- rays to silver is ***Leaching*** process.

Leaching: Leaching is the process by which constituents of a solid particles are released into a contacting liquid phase.

Chemical double displacement reactions which is involved in the conversion of x – rays into silver using concentrated nitric acid are:

$$Ag + HNO3 \rightarrow AgNO3 + NO2 + H2O$$

After adding salt solution, silver nitrate reacts with sodium chloride and forms silverchloride as precipitate.

$$AgNO3 + NaCl \rightarrow AgCl + NaNO3$$

Chemical double displacement reaction which is involved in the conversion of x – rays into silver using concentrated sodium hypochlorite is that sodium hypochlorite reactswith silver bromide of x – ray photographic film emulsion and results in the formation of silver chloride which precipitates and the reaction is:

$$2AgBr + 2NaClO \rightarrow 2AgCl + 2NaBr + O2$$

Chemicals

Nitric Acid: Concentrated nitric acid (HNO3) is used to recover the silver from wastex – rays.

Sodium hypochlorite: Concentrated Sodium hypochlorite (NaClO) which is alsocalled as Bleach solution is used to recover the silver.

Preparation of chemical solution:

- **Salt solution:** 5 grams of salt (NaCl) were taken and dissolved in 20 ml (0.25 w/v %) of deionized water.
- **Nitric acid (Concentrated)** - 500 ml
- **Sodium Hypochlorite (Bleach solution**) - 500 ml

3. EXPERIMENTAL PROCEDURE

1. Experimental procedure of recovery of silver from waste x- rays using Nitric acidsolution

Collect waste x – ray films and cut them into small pieces. Note the weight of film pieces weight using weighing balance. Take 500 ml beaker and pour 300 ml of concentrated Nitric acid (HNO3) into the beaker. Dip the x – ray film pieces into beaker until the film pieces become colourless. Keep the dipped x – ray film pieces in a water. Keep the beaker undisturbed for 30 minutes. Pour 20 ml of deionized water into another beaker and add

5 grams of salt into the beaker. Stir the solution until the salt completely dissolves in the water. After 30 minutes, add salt solution into the beaker which contains nitric acid solution. Filter the solution using filter paper. Take the precipitate which is settled at the bottom of the beaker into a filter paper and dryit for one hour. Note the weight of the dried silver precipitate. Now take the dried silver precipitate into crucible and burn it using a gas burner. The silver has been recovered. Note the weight of the recovered silver.

Fig-1: X- ray film pieces after dipping into nitric

Fig-2: Dipped X- ray pieces in water

Fig-3: Nitric acid solution after adding salt

Fig-4: Silver chloride precipitate at the bottom of the beaker

Fig-5: Filtering the solution with filter paper

Fig-6: Dried silver chloride precipitate

Fig-7: Burning the silver precipitate in a crucible using gas burner

Fig-8: Recovered silver

2. Experimental procedure of recovery of silver from waste x- rays using Sodiumhypochlorite solution

Collect waste x- ray films and cut them into small pieces. Note the weight of x-ray film pieces using weighing balance. Take a 500 ml beaker and pour 500 ml of concentrated Sodium hypochloritesolution which is also known as Bleach solution (NaClO). Dip the x- ray film pieces into the beaker until the film pieces become colourless. Leave the beaker undisturbed for seven hours. After seven hours, silver chloride precipitate is formed at the bottom of the beaker. Filter the solution using filter paper. Take the silver chloride precipitate into a filter paper and dry it for one hour. After drying, note the weight of dried silver precipitate. Take a dried silver precipitate into crucible and burn it using gas burner. The silver has been recovered. Note the weight of the recovered silver.

Fig-9: Concentrated Sodium hypochlorite solution (Bleach solution)

Fig-10: Silver chloride precipitate

Fig-11: Dried silver chloride precipitate

Fig-12: Burning silver precipitate using gas burner

Fig-14: Recovered silver

4. Result

Weights occurred by using Nitric acid:

a. Weight of pure recovered silver = 0.45 g
b. Weight of prepared film = 66 g
c. Weight of dried silver precipitate = 0.575 g

Weights occurred by using Sodium hypochlorite:

a. Weight of pure recovered silver = 1.95 g
b. Weight of prepared film = 285 g
c. Weight of dried silver precipitate = 2.75 g

4.1. Yield percentage of recovered silver

The yield percentage of recovered silver was calculated by using the formula given below.

$$\text{Percentage of yield of recovered silver} = \left(\frac{\text{weight of pure recovered silver}}{\text{Weight of prepared film}}\right) * 100 \rightarrow (1)$$

During the measurement of yield, the weight of used x-ray film is taken as input and the weight of pure recovered silver is used as output. There was a considerable variation in the amount of silver recovered irrespective of the size and type of the x – ray film. This fact is due to the dependency of the area covered by the x – ray image on the surface of the entire film.

$$\text{Percentage of yield of recovered silver using Nitric acid } (HNO3) = \left(\frac{0.45}{66}\right) * 100$$

= 0.68%

$$\text{Percentage of yield of recovered silver using Sodium hypochlorite } (NaClO) = \left(\frac{1.95}{285}\right) * 100$$

= 0.68 %

4.2. Recovery percentage of recovered silver

The recovery percentage of silver recovered was calculated by using the formula given below.

$$\text{Percentage of recovery of recovered silver} = \left(\frac{\text{Weight of pure recovered silver}}{\text{Weight of dried silver precipitate}}\right) * 100 \rightarrow (2)$$

During the measurement of recovery percentage, the weight of used dried silver precipitate is taken as input and the weight of pure recovered silver is used as output.

$$\text{Percentage of recovery of recovered silver using Nitric acid (HNO3)} = \left(\frac{0.45}{0.575}\right) * 100$$

$$= 78.2\ \%$$

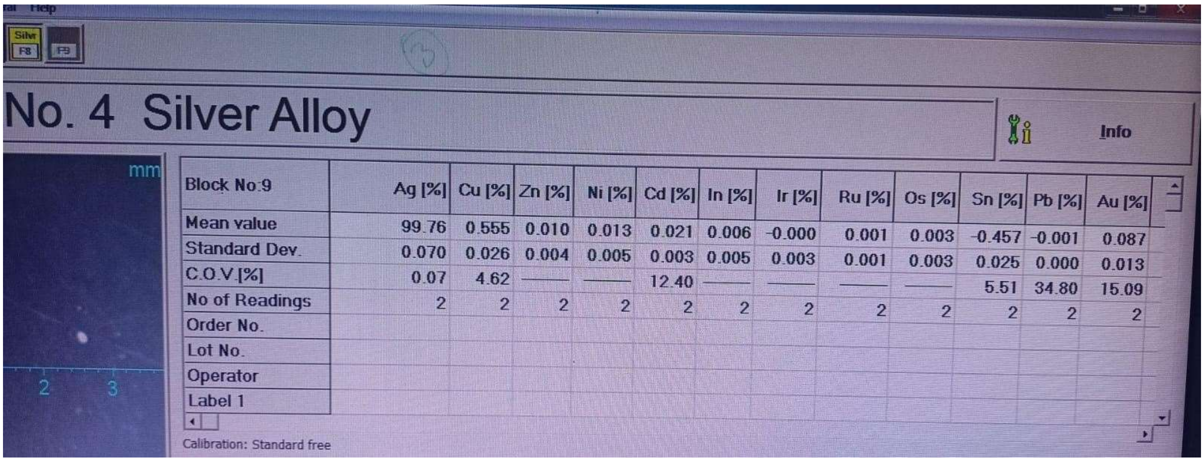
$$\text{Percentage of recovery of recovered silver using Sodium hypochlorite} = \left(\frac{1.95}{2.75}\right) * 100$$

$$= 71\ \%$$

4. 3. Purity of recovered silver

The purity of recovered silver was tested at *Perfect Gold Skin Testing Centre* which is located at Mahaldar Street, Ananthapuramu.

Fig-14: Certificate of purity of silver recovered from Nitric acid

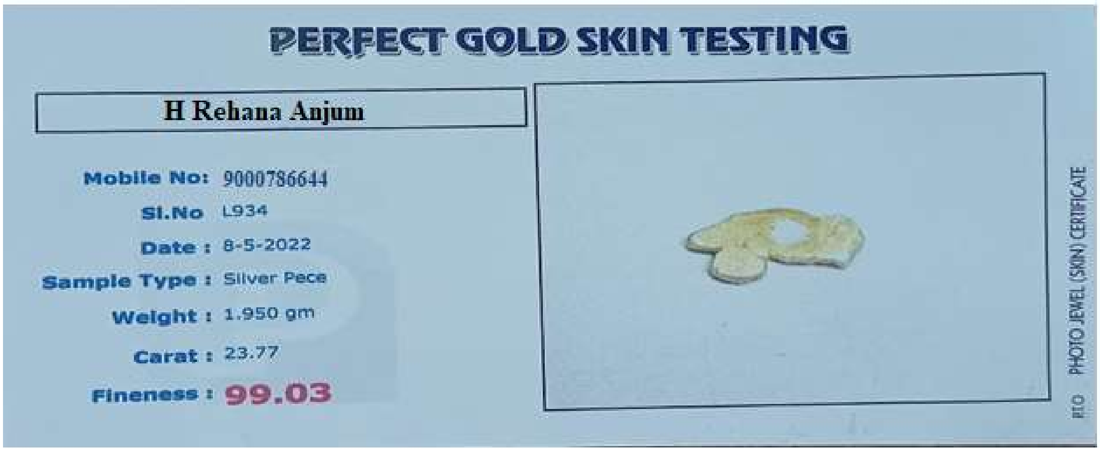


No. 4 Silver Alloy

Block No:9	Ag [%]	Cu [%]	Zn [%]	Ni [%]	Cd [%]	In [%]	Ir [%]	Ru [%]	Os [%]	Sn [%]	Pb [%]	Au [%]
Mean value	99.76	0.555	0.010	0.013	0.021	0.006	-0.000	0.001	0.003	-0.457	-0.001	0.087
Standard Dev.	0.070	0.026	0.004	0.005	0.003	0.005	0.003	0.001	0.003	0.025	0.000	0.013
C.O.V.[%]	0.07	4.62	——	——	12.40	——	——	——	——	5.51	34.80	15.09
No of Readings	2	2	2	2	2	2	2	2	2	2	2	2
Order No.												
Lot No.												
Operator												
Label 1												

Calibration: Standard free

Fig-15: Composition (purity and impurities) of recovered silver from Nitric acid



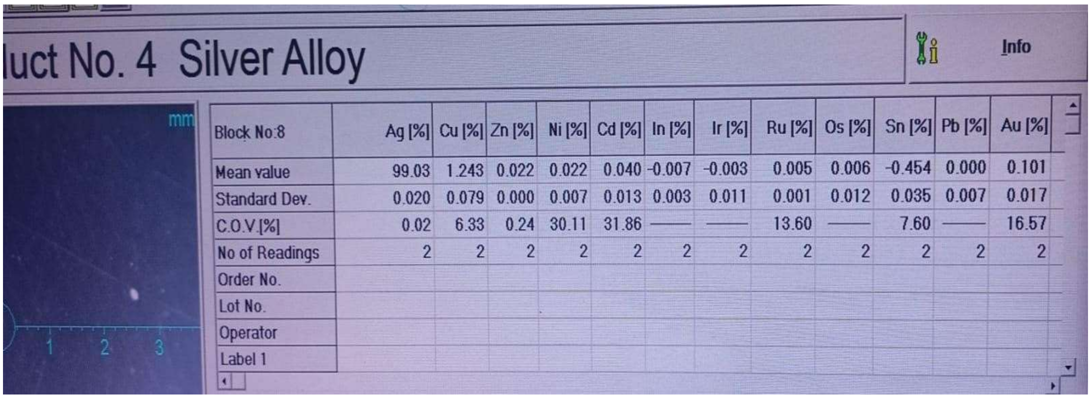
PERFECT GOLD SKIN TESTING

H Rehana Anjum

Mobile No: 9000786644
Sl.No L934
Date : 8-5-2022
Sample Type : Silver Pece
Weight : 1.950 gm
Carat : 23.77
Fineness : 99.03

PHOTO JEWEL (SKIN) CERTIFICATE

Fig-16: Certificate of purity of silver recovered from Sodium hypochlorite solution



luct No. 4 Silver Alloy

Block No:8	Ag [%]	Cu [%]	Zn [%]	Ni [%]	Cd [%]	In [%]	Ir [%]	Ru [%]	Os [%]	Sn [%]	Pb [%]	Au [%]
Mean value	99.03	1.243	0.022	0.022	0.040	-0.007	-0.003	0.005	0.006	-0.454	0.000	0.101
Standard Dev.	0.020	0.079	0.000	0.007	0.013	0.003	0.011	0.001	0.012	0.035	0.007	0.017
C.O.V.[%]	0.02	6.33	0.24	30.11	31.86	——	——	13.60	——	7.60	——	16.57
No of Readings	2	2	2	2	2	2	2	2	2	2	2	2
Order No.												
Lot No.												
Operator												
Label 1												

Fig-17: Composition (purity and impurities) of recovered silver from Sodium hypochlorite solution

5. Discussion

In this research work the silver which is recovered using concentrated Nitric acid is 99.76 % pure silver with 23.94 carat. The weight of recovered silver is 0.45 grams. The silver consists of 0.24%impure metals like copper, zinc, nickel etc. And the silver which is recovered using Concentrated Sodium hypochlorite solution (also known as Bleach solution) is 99.03 % pure silver with 23.77 carat. The weight of recovered silver is 1.95 grams. The silver consists of 0.97% impure metals like copper, zinc, nickel etc.

In 2020, Prof. D. K. Chandre and Vivek Virendra Mishra have done their research on silver recovery from used x-ray film using borax compound. They used sodium hydroxide and ethanol. They concluded that with the use of stripping process of sodium hydroxide we can get maximumyield with better purity. The stripping process of sodium hydroxide is eco-friendly as it does not produce any harmful compounds [9].

In 2019, Carlos Alberto has done his research on recovering of silver from waste x – rays using chemicals like Sodium Hydroxide and Sodium Hypochlorite. He concluded that Sodium hypochlorite was the best option for the extraction of silver containing metal in fixator, being this 21% more efficient than Sodium hydroxide [10].

In 2017, Anuradha Jabasingh has done her research on recovery of silver from waste x – ray films using chemicals such as sodium sulphide, hydrochloric acid, Sodium hydroxide, borax dehydrates, sodium carbonate procured from sigma – Aldrich. She concluded that increasing concentration of sodium hydroxide beyond 1.5 M resulted in a difficulty of silver recovery due toprecipitation. Very high temperatures are not suitable for the silver stripping. She finally concluded that optimum recovery conditions of silver were stripping temperature of 70.88°c, stripping time of 10.97 min, and sodium hydroxide concentration of 1.46 M. Silver from used x-rays had a purity of 98.28% [11].

In 2015, Jayant P. Parpalliwar, Pallavi S. Patil have done research on recovery of silver from waste x rays using protease enzyme. They used enzymes from Bacilus subtilis. They concluded that silver was successfully recovered in good yield from photographic films by the enzymatic method. The method is easy but it has advantages such as bad smell and burning step at high temperatures. Otherwise, the enzyme obtained from Bacilus subtilis NCIM 2724 is not thermophilic and its activity is high at a pH near neutral. The thermophilic and alkaliphilic enzymes will yield good result in the stripping of gelatine- silver layer [12].

In 2012, A. D. Bas, H. Deveci have done research on recovery of silver from x ray film processing effluents by hydrogen peroxide treatment. They concluded that treatment of waste x - rays with hydrogen peroxide are a highly exothermic process because of side reactions. IncreasingpH appeared to improve the recovery of silver discernibly at low levels of hydrogen peroxide. The addition of ethyl glycol was shown to enhance the silver recovery apparently due to its stabilizing effect on hydrogen peroxide. It can be inferred from this study that hydrogen peroxideas a green chemical is potentially a suitable reagent for the treatment of x – rays photo processing effluents allowing the recovery of silver as well as the removal of thiosulphate [13].

In 2010, S. Shankar and R. Seeta Laxman have done their research on recovery of silver from waste x- rays by alkaline protease from *Conidiobolus Coronatus.* They concluded that the loss inweight of x ray films after the treatment was around 5% (w/w) based on initial weight. The silvercontent in hydrolysate was determined by atomic absorption and corresponded to 3.87% (w/w) solid sludge. Silver from the hydrolysate was recovered either as metallic silver or as silver chloride [14].

6. Conclusion

The current project is an effort towards the recovery of silver from waste x- ray photographic films. Recovering of silver from waste x – rays using chemicals such as nitric acid and sodium hypochlorite is a reliable and easy method as it is economically convenient and effectively uses waste x- rays which are considered as hazardous waste. Reuse or recycle of natural mineral resources remains most feasible option to slow down the exhaustion caused to their depletion. By the use of recovery process to get maximum benefits like we reduce the solid waste which can be generated by the used X- ray films and we get the precious metal Silver. We used chemical precipitation technique for the recovery of silver which needs less heat. Nitric acidand sodium hypochlorite were used as leaching agents. In the process of recovery of silver using nitric acid we added salt solution to form silver chloride as precipitate. X – Ray films contain 1.5% - 2% of pure silver which can be recovered and reused. It contains silver as emulsion whichis the combination of gelatin and halide.

- In the process of recovery of silver using sodium hypochlorite, silver bromide in the film reacts with sodium hypochlorite and forms silver chloride as precipitate.
- The factors influencing the percentage of recovery of silver are leaching time and acid concentration. Increasing the acid concentration and leaching time percentage of recovery of silver increases.
- Chemical precipitation process has many advantages such as low cost and easily monitored.
- We observed that the recovered silver using the chemical precipitation process has no toxicity levels and high purity.
- We also observed that the purity of recovered silver from waste x- rays using nitric acid is 99.76% with 23.94 carat and the purity of recovered silver from x- rays using sodium hypochlorite is 99.03% with 23.77 carat.

- Percentage of yield of recovered silver is 0.68% which is same for both nitric acid solution and sodium hypochlorite solution that are used as leaching agents to recover the silver.

We conclude that percentage of recovery of silver is more for nitric acid (78.2%) than the sodium hypochlorite solution (71%). The high purity of silver can be recovered from nitric acid (99.76%) than the sodium hypochlorite solution (99.03%). The silver which is recovered from sodium hypochlorite solution consists of more impure metals than from nitric acid solution.

Reference

1. https://www.rsc.org/periodic-table/element/47/silver
2. http://ijariie.com/AdminUploadPdf/Silver_recovery_from_used_x_ray_film_using_borax_compound_ijariie4329.pdf
3. https://www.jewelryshoppingguide.com/different-types-of-silver-jewelry/
4. https://www.alexmakina.com/what-are-the-types-of-silver
5. Encyclopedia of Science and Technology (1976) Vol. 5, Van Nostrand, New York, pp. 595–596.
6. A. D. Bas, E. Y. Yazici, and H. Deveci, (2012) "Recovery of silver from X-ray film processing effluents by hydrogen peroxide treatment," Hydrometallurgy, vol. 121– 124, pp.
7. N. Sathaiyan, P. Adaikkalam, J. A. M. A. Kader, and S. Visvanathan, (2001)"Silver Recovery from Photographic Process Wastes," in Encyclopedia of Materials: Science and Technology (Second Edition), K. H. J. Buschow, R. W. Cahn, M. C. Flemings, B.Ilschner, E. J. Kramer, S. Mahajan, et al., Eds., Ed Oxford: Elsevier, pp. 8621-8623.
8. WEEDON, KAYE (1945): Report on Silver Recovery and Regeneration of Fixing Bath, Oslo (private communication).
9. https://iopscience.iop.org/article/10.1088/1757-899X/294/1/012007
10. http://journal-repository.com/index.php/ijaers/article/view/1033
11. https://www.scribd.com/document/492066249/186788-Article-Text-474888-1-10-20190524
12. https://bipublication.com/files/IJABR-V6I2-2015-9_Jayant%20P.%20Parpalliwar.pdf
13. https://www.academia.edu/2534875/Recovery_of_silver_from_X_ray_film_processing_effluents_by_hydrogen_peroxide_treatment
14. https://www.researchgate.net/publication/303015785_Recovery_of_Silver_from_Waste_X-Ray_Film_by_Alkaline_Protease_from_Conidiobolus_coronatus